

# Annular Denuder Coatings for the Collection of Organic Vapor Phase During PM<sub>2.5</sub> Sampling

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# Particulate Matter (PM)

- Size – 0.005 to 50 $\mu\text{m}$ 
  - PM10
    - Coarse 2.5 $\mu\text{m}$  – 10 $\mu\text{m}$
    - PM2.5 fine fraction
    - Ultrafine 1 $\mu\text{m}$
- Mass
  - 2 to 200 $\mu\text{g}/\text{m}^3$
- Composition
  - $\text{SO}_4$ ,  $\text{NH}_3$ ,  $\text{NO}_3$ , EC/OC, PAH

# Particulate Matter Sources

- Coarse - PM10
  - Dust, sea salts, vehicles, combustion products
- Fine – PM2.5
  - Vehicles emissions, oil & coal utility, wood fuel, biomass burning
- Primary Emissions
  - Transportation, fuel combustion, road dust, construction
- Secondary Aerosol Formulation
  - Sulfates, nitrates, organic particulates from VOCs

# Problems Associated With PM

- Health effects
  - Inhalables (PM10) – the larger particles get trapped in bronchial tubes of upper respiratory tract
  - Respirables (PM2.5) – the smaller the particle the deeper into the lungs it can penetrate
  - Possible linkage to chronic bronchitis and asthma

# Need for Speciation

- Characterization of metals, ions, and carbon constituents
- Air quality modeling analysis
- Aiding in health studies
- Understanding the effects of atmospheric constituents
- Aid in monitoring network design by USEPA

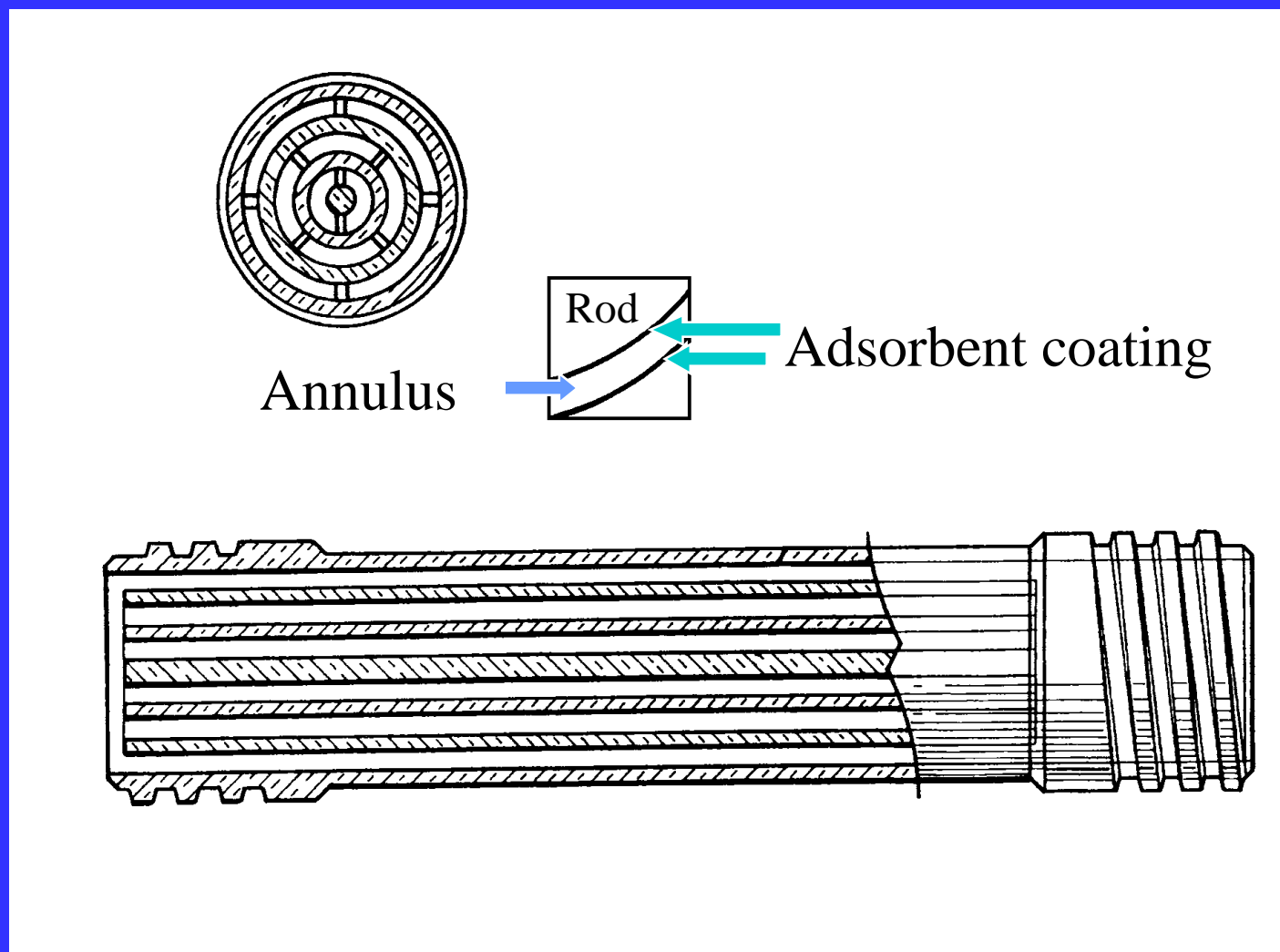
# Analytical Speciation Methodology for PM

- Analytical Method
- Gravimetric
- Ion Chromatography
- Thermal/Optical Method-  
NIOSH 5040
- EDXRF, ICP, AA
- Analyte
- Total Mass
- $\text{SO}_4$ , Cl,  $\text{NH}_4$ ,  $\text{NO}_3$
- EC/OC
- S, Al, Si, Ti, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Ba, Pb, metals

# Denuder Technology

- Denuder Types
  - Single channel or multi channel denuders
  - Glass, metal, ceramic
  - Annular – typically 1mm annulus
  - Honeycomb
- Coated
- Many times placed in series
- Extracted for the analysis
- Can be recoated and reused
- Often used as a “scrubber”

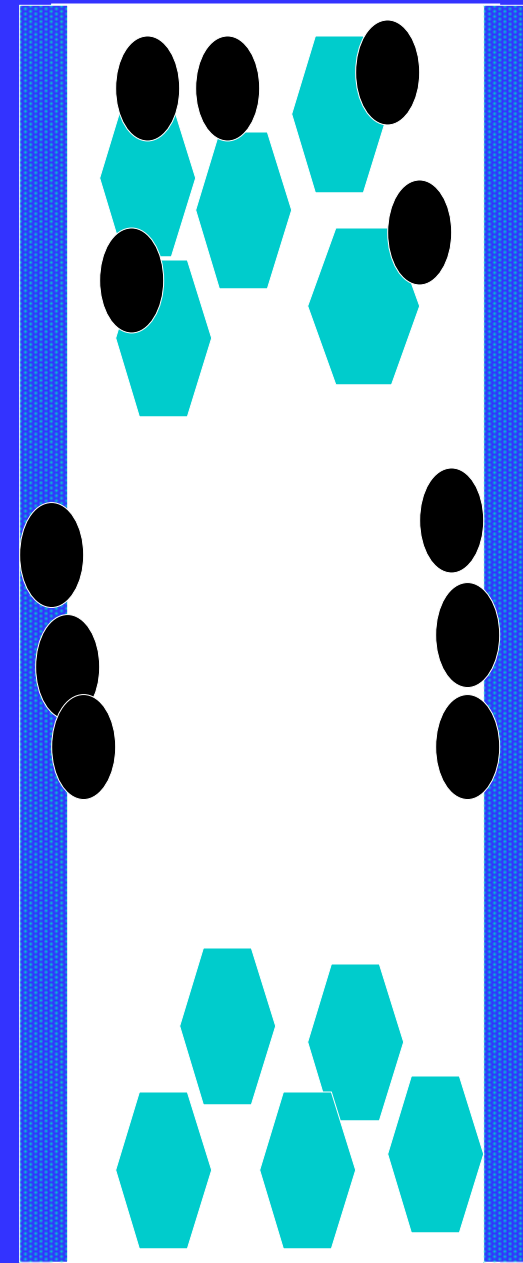
# Multi Channel Annular Denuder





# How Denuders Work

- The vapor phase of the particulate is adsorbed onto the adsorbent material coated on the walls of the denuder.
- Stripped particulate is collected downstream.
- Denuder is solvent rinsed to extract vapor phase.



# Denuder Types



## Denuder Types cont.



# Common Denuder Coatings

- Coating

- Citric acid

- $\text{Na}_2\text{CO}_3$

- $\text{MgO}$

- XAD-4

- Analytes

- $\text{NH}_3$

- $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$

- Nitric acid scrubber

- SVOCs-PAH

## Organic PM<sub>2.5</sub> Speciation

- Vapor phase of particulate is denuded from particle. Vapor phase has a higher partitioning coefficient.
- Partitions in adsorbent coated on walls
- Can be extracted and analyzed
- For semi-volatiles technology not fully developed
- PAHs commonly extracted using XAD-4

## XAD-4 Physical Characteristics

- Styrene divinylbenzene copolymer
- High surface area – 780m<sup>2</sup>/g
- Average pore size 50Å

# Denuder XAD-4 Coating Requirements

- Milled to 1-2 $\mu$ m
- Soxhlet extraction cleaned
- Vacuum oven dried
- Crosslinking agents added prior to coating
- Uniform deposition
  - Ensure laminar flow
  - Decrease turbulence
  - Affect efficiency of sampling
- Sample capacity

# XAD-4 Denuder Coating

- Dr. Lara Gundel at LBNL has developed a procedure for coating glass annular denuders with XAD-4.
- Slurry of XAD-4 in Hexane
- Fill denuder, roll or invert, remove, dry, weigh, repeat 10 times
- US Patent 5,763,360
- Licensing agreement



# Comparison of Gundel/Restek Coatings

- XAD-4
- 52mm x 285mm 8 Channel denuders
- LBL denuders coated by Dr. Lara Gundel
- Restek coated using a 1 step coating procedure, vacuum oven dried
- Samples taken at Houston EPA Supersite  
September 2000
- 2 denuders in series

Sample collected during Texas Air Quality Study 2000 at LaPorte,  
Collection period - September 10,2000 from 00:00 to 11:30 AM

	[] ng/m <sup>3</sup>			
LBL denuders	front denuder		back denu	front/total
Name	1st wash	2nd wash	1st wash	lbl
phenol	12	0	16	43%
Naphthalene	11	0	23	32%
nC12	9	0	0	100%
nC13	10	0	0	100%
1-methyl naphthalene	12	0	0	100%
2-Methyl naphthalene	6	0	1	89%
Biphenyl	2	0	0	100%
Dimethyl naphthalene	2	0	0	100%
acenaphthene	3	0	0	100%
Dibenzofuran	4	0	0	100%
nC16	4	0	0	100%
fluorene	4	0	0	100%
nC17	4	0	0	93%
phenanthrene	8	0	0	100%
anthracene	8	0	0	96%
nC19	1	0	0	100%
nC20	1	0	0	100%
fluoranthene	2	0	0	100%
nC21	1	0	0	100%
pyrene	0	0	0	100%

	[] ng/m <sup>3</sup>			
Restek denuders	front denuder		back denu	front/total
Name	1st wash	2nd wash	1st wash	
phenol	25	0	25	49%
Naphthalene	23	0	25	49%
nC12	9	0	0	100%
nC13	10	0	0	100%
1-methyl naphthalene	15	0	0	100%
2-Methyl naphthalene	8	0	0	100%
Biphenyl	2	0	0	100%
Dimethyl naphthalene	2	0	0	100%
acenaphthene	4	0	0	100%
Dibenzofuran	4	0	0	100%
nC16	4	0	0	100%
fluorene	4	0	0	100%
nC17	5	0	0	100%
phenanthrene	7	0	0	100%
anthracene	7	0	0	100%
nC19	1	0	0	100%
nC20	1	0	0	100%
fluoranthene	1	0	0	100%
nC21	1	0	0	100%
pyrene	0	0	0	100%

Comparison of Front Denuder % recovery		
Name	LBL	Restek
phenol	43%	49%
Naphthalene	32%	49%
nC12	100%	100%
nC13	100%	100%
1-methyl naphthalene	100%	100%
2-Methyl naphthalene	89%	100%
Biphenyl	100%	100%
Dimethyl naphthalene	100%	100%
acenaphthene	100%	100%
Dibenzofuran	100%	100%
nC16	100%	100%
fluorene	100%	100%
nC17	93%	100%
phenanthrene	100%	100%
anthracene	96%	100%
nC19	100%	100%
nC20	100%	100%
fluoranthene	100%	100%
nC21	100%	100%
pyrene	100%	100%

## *XAD-4 As an Organic Scrubber*

- *XAD-4 coated on metal denuder*
- *Total carbon test on quartz filter*
- *NIOSH 5040 method*
- *Sunset Labs Instrument Thermal Optical Analyzer*

16 liter/min



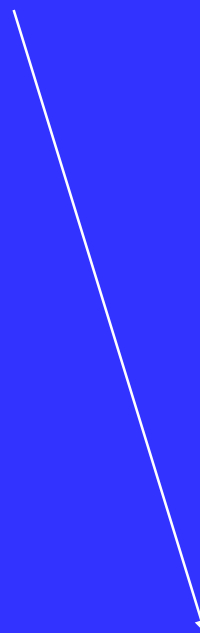
Teflon filter



XAD-4 Denuder

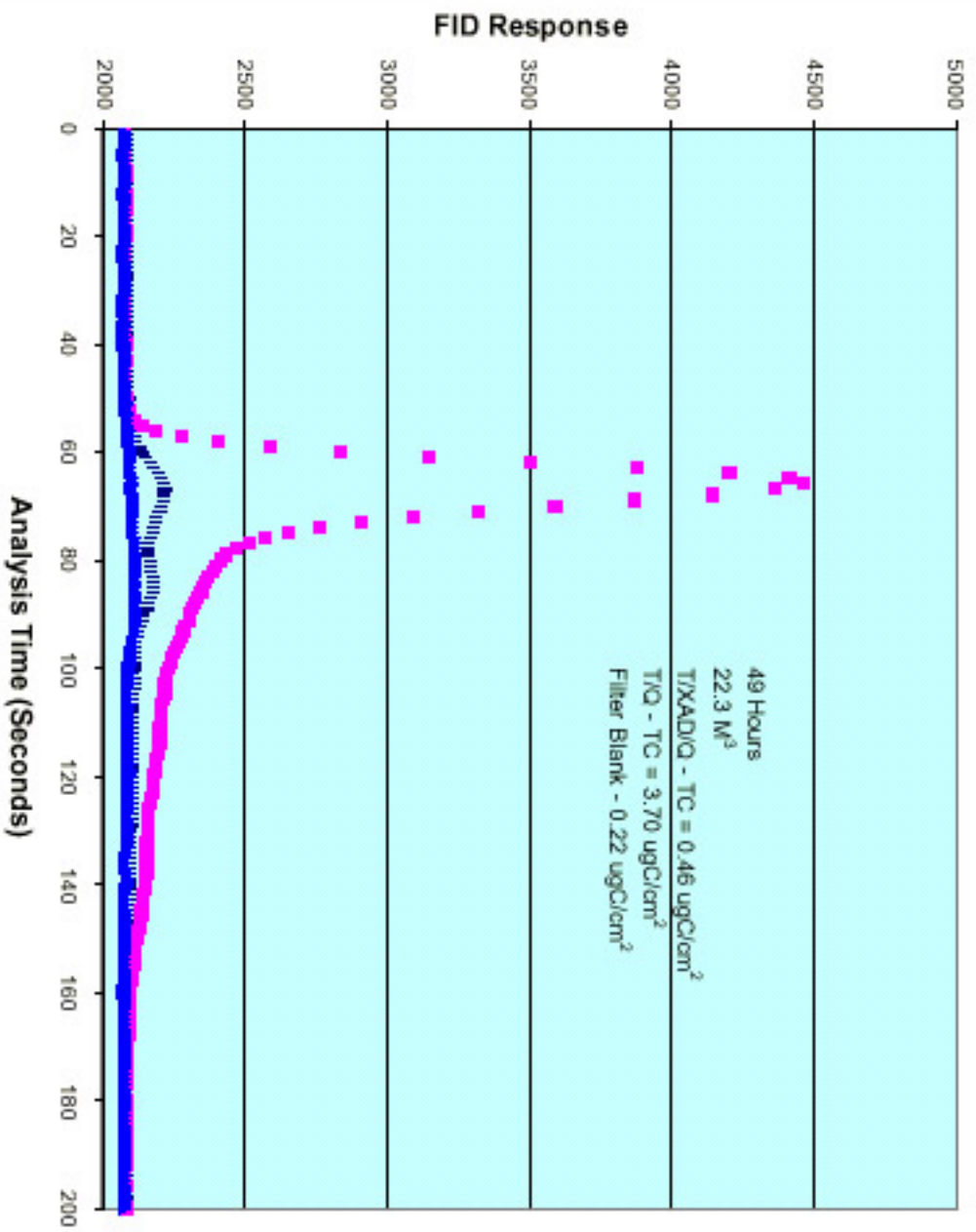


quartz



quartz

# TC Analysis On Quartz



■ Teflon/XAD Front  
■ Teflon Front Only  
▲ Filter Blank



# Future Research

- Non-particulate coating
  - Non-particulate porous film
  - Elimination of carbon artifact for TC
  - Eliminate particles bias
  - Ability to dope for selectivity
- Carbon coating
  - Great organic scrubber



# Photo of Non-Particulate Coated Denuder



## Conclusion

- Denuders technology has become an important part of PM<sub>2.5</sub> speciation.
- XAD-4 is currently being evaluated for organic speciation such as PAHs.
- More research is needed to find more selective coatings for organic speciation of classes of compounds.

# Acknowledgements

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